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Mechanics of carbon nanotubes and their polymer composites

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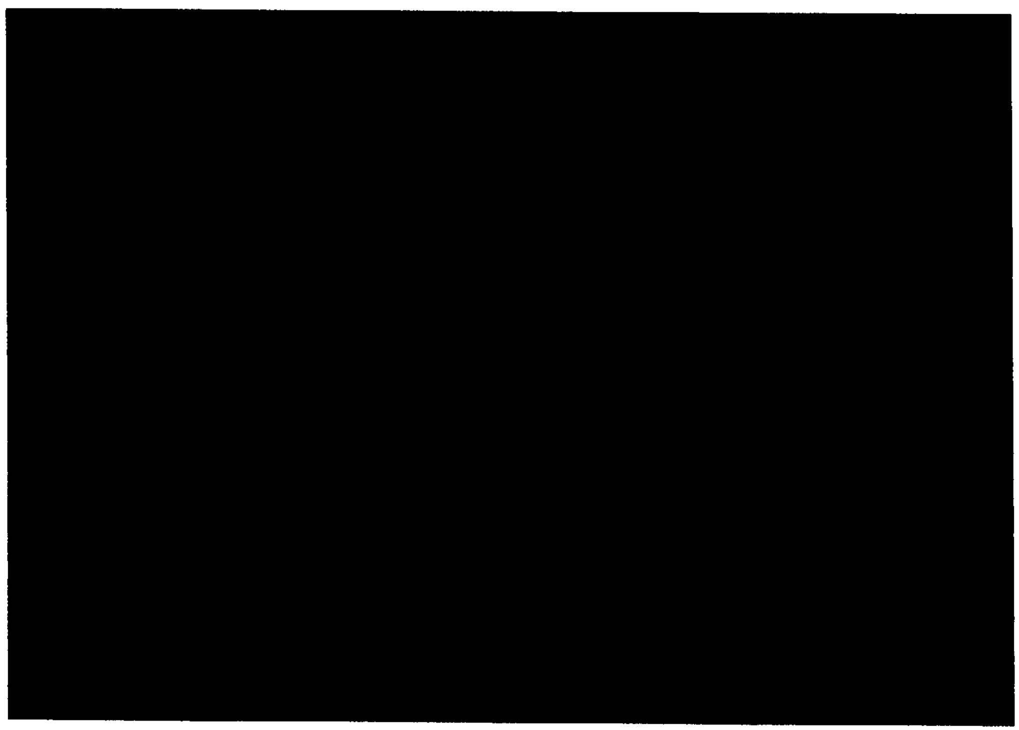
Carbon Nanotube: Structures

Atomic structure:

Quasi one dimensional; C-C bond length 1.43 A;

Radius ~ Nanometer; Length ~ μm (current upper range); Index (n,m)



Application of Carbon Nanotubes

Nano fibers: Strong mechanical properties

Nano devices: Wide variety of electronic properties and mechanical-electronic couplings

Nano sensors: Physical and Chemical adsorption of gas molecules, ions

Simulation Methods

(1) Molecular Dynamics: Newton's Equation

Force Field for Carbon nanotubes:

Tersoff Brenner potential, fitted to carbon and hydrocarbon systems, 3-body type, bond broken and formation

(2) Tight Binding method

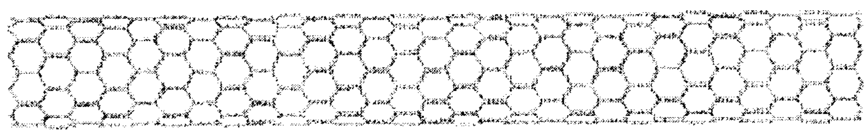
(3) Ab initio method (Density Functional theory)

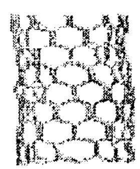
Elastic Properties of Carbon Nanotubes

Small strain: uniform deformations, elastic behavior
continuum theory applicable

Large strain: local deformations, defects, dislocations

Tension, Compression, bending, and (Torsion):





Yield Strain of CNT

Tension

Simulation: 30% yield strain from fast strain rate (1/ps) molecular dynamics simulations (B.I. Yakobson et.al. Comput. Mater. Sci. 1997)

Experiments: 6% maximum strain in SWCNT ropes; 12% maximum strain in MWCNTs (D.A. Walter et al, Appl. Phys. Lett. 1999; M.F. Yu et al, Phys. Rev. Lett. and Science 2000)

Compression

Simulation:

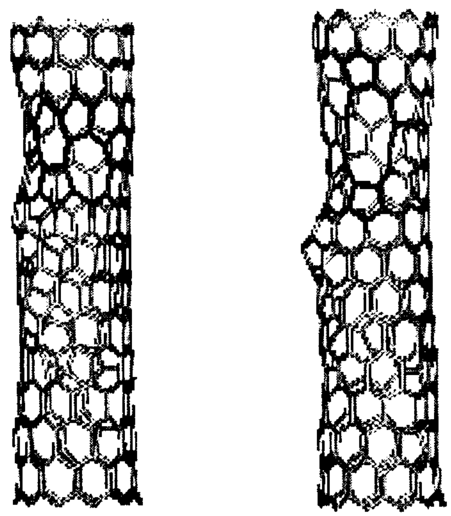
T=0K, Tersoff-Brenner potential: Super-elastic up to 20%

T=0K, Tight Binding: diamond like defects, collapsed at 12%

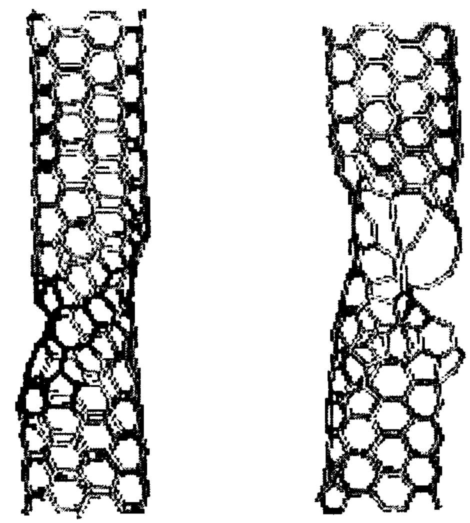
Experiment:

Collapsing of CNT within polymer matrix under compression stress 150GPA (TEM study)

Yielding under Tensile Stress



11.5% tensile strained
CNT (10,0), T=1600K

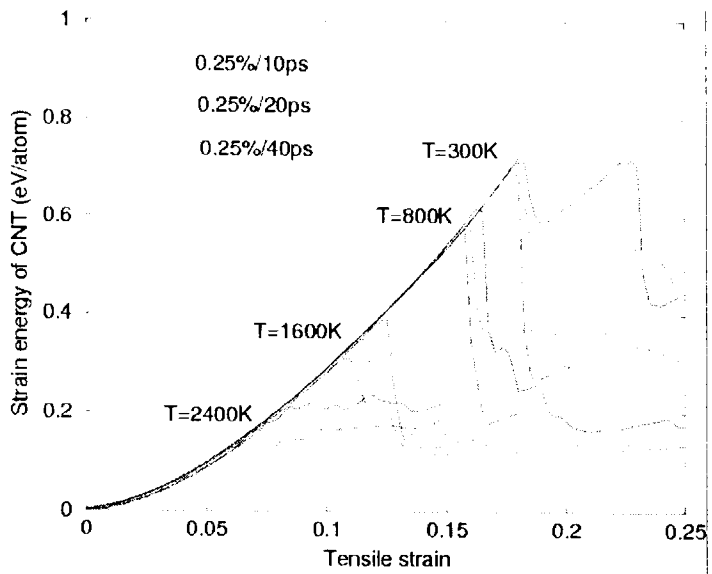


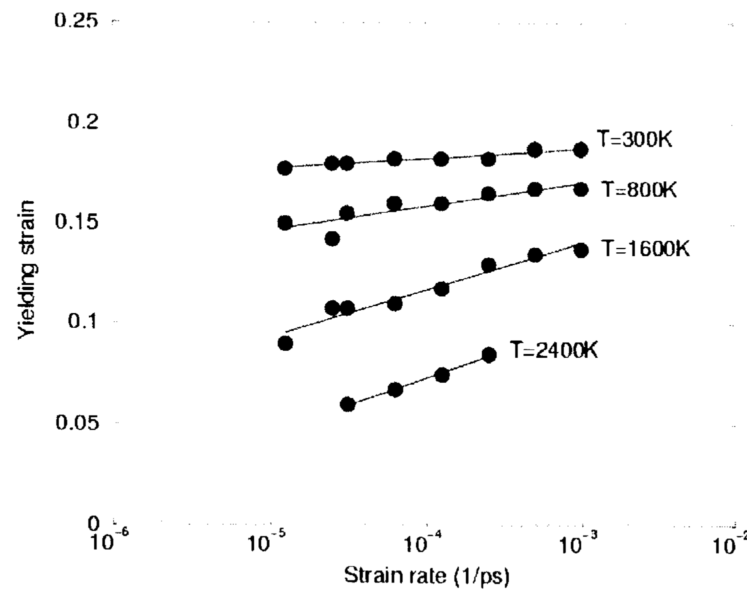
9% tensile strained
CNT (5,5), T=2400K

* D. Srivastava, C. Wei, and K. Cho, Appl. Mech. Review (2002)

Yielding: Strain-rate and Temperature Dependence

Tensile strain applied to a 60Å long (10,0) CNT





- Yielding: strongly dependent on strain rate and Temperature

- Linear dependent on temperature of the slope of yield strain vs. strain rate : Activated Process

Yield Strain under Tension

$$\varepsilon_Y = \frac{\bar{E}_\nu}{VK} + \frac{k_B T}{VK}\ln\left(\frac{N\dot{\varepsilon}}{n_{site}\dot{\varepsilon}_0}\right)$$

$\dot{\varepsilon}$: Strain rate; $\dot{\varepsilon}_0$: Constant related with vibrational frequency

K : Force constant; V: Activation volume; $\bar{E}_\nu$: Activation energy

N : Number of process involving in yielding; n_{site} : Site available

Length effect:

$$\Delta\varepsilon_Y = -\frac{k_B T}{VK}\ln(n_{site}/n^0_{site})$$

Temperature effect:

$$\left(\frac{\dot{\varepsilon}_1 N}{n_{site}\dot{\varepsilon}_0}\right)^{T_1} = \left(\frac{\dot{\varepsilon}_2 N}{n_{site}\dot{\varepsilon}_0}\right)^{T_2}$$

Yielding at Realistic Conditions

- *Parameters obtained from fitting of MD simulations' data*

$\overline{E}_v = 3.6\text{eV}; \qquad V = 2.88\,\overset{\circ}{A}{}^{3}$

$\frac{\dot{\varepsilon}_0}{N} = 8 \times 10^{-3}\ ps^{-1}$

- *Experimental feasible conditions*

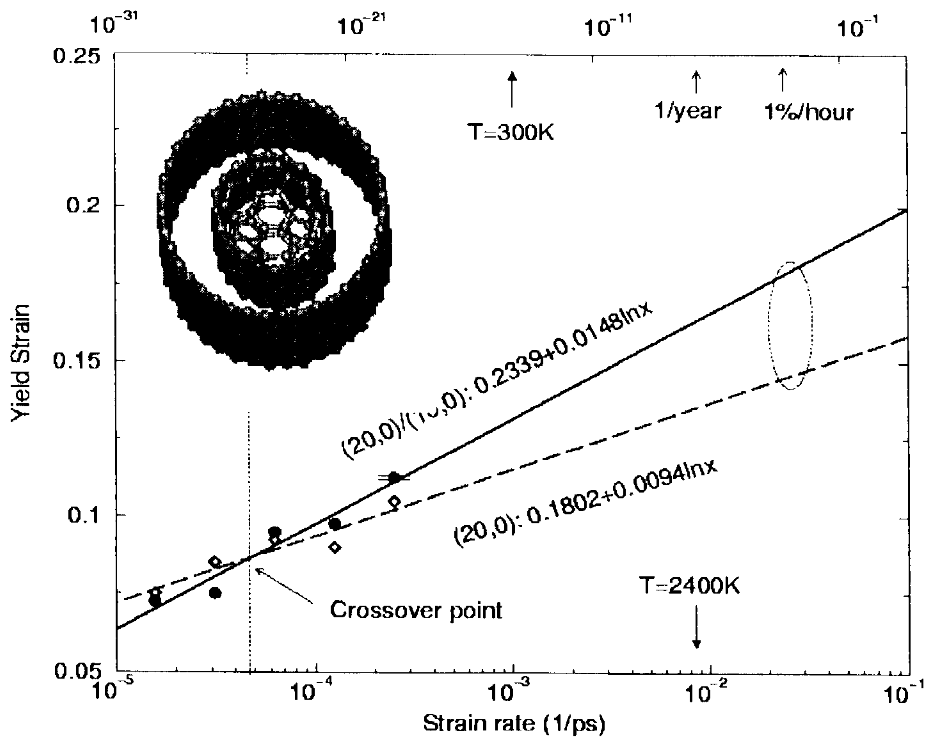
length ~ 1μm; strain rate ~ 1%/hour; T ~ 300K

$\Longrightarrow$ Yield strain: 9 ± 1 %

Maximum tensile strains from experiments:
5-6 % for SWCNT ropes; 12% for MWCNTs

* D.A. Walter, et. al. , Appl. Phys. Lett. V74, 3803 (1999)
M.-F. Yu et.al. Phys. Rev. Lett., V84, 5552 (2000); M.-F. Yu et. al., Science, V287, 637 (2000)

Yielding of MWCNT



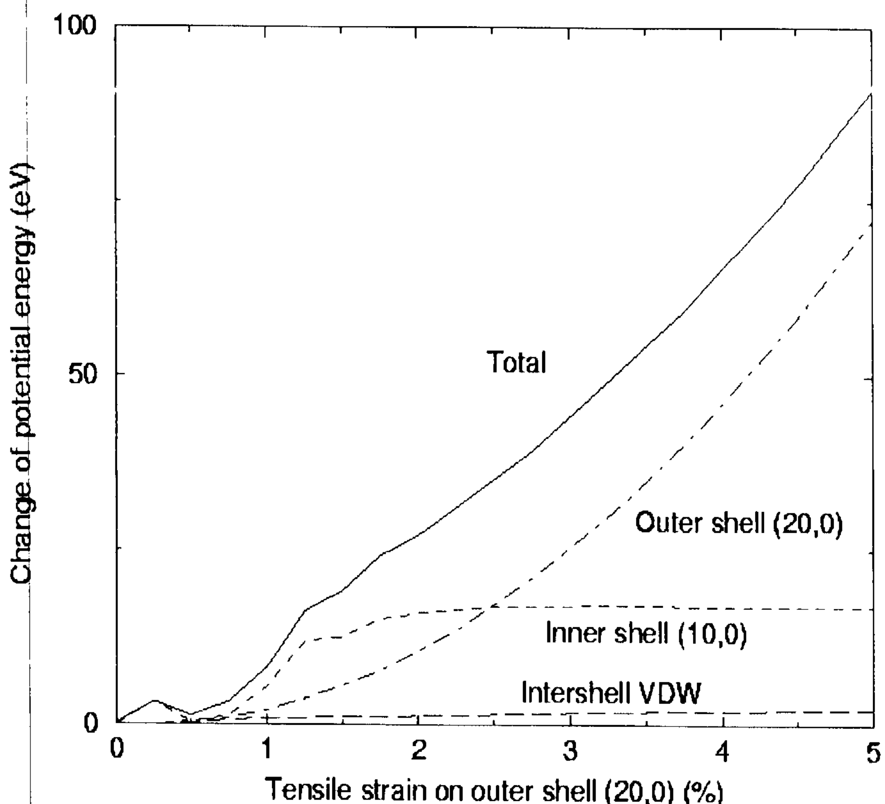
(1) For $\dot{\varepsilon}$ = 1%/hour, and T=300K

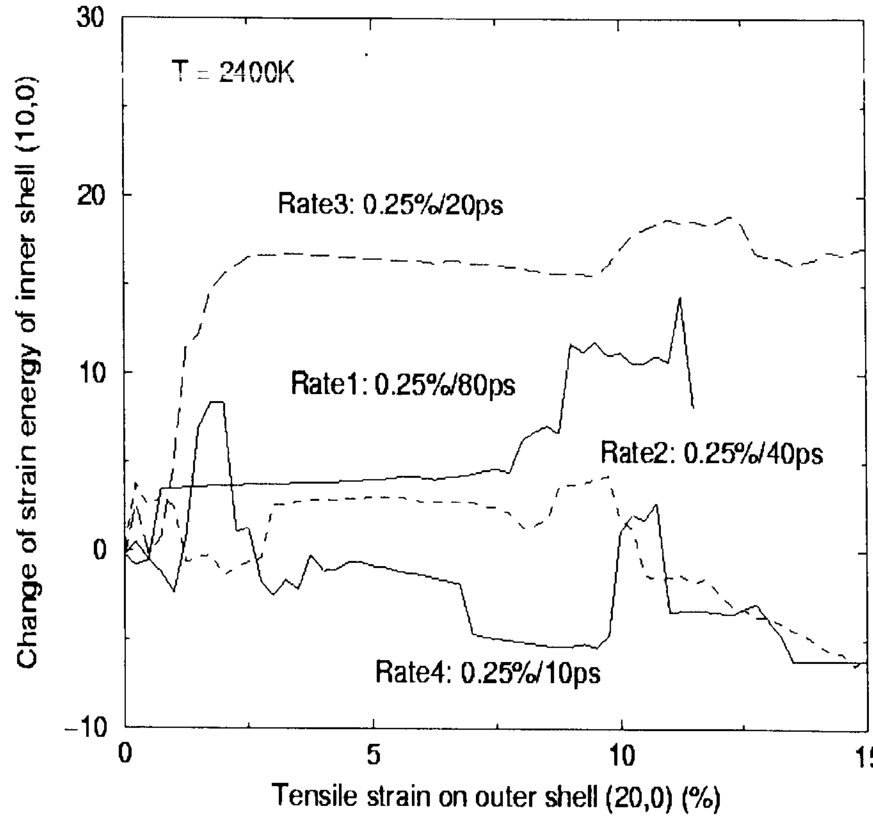
ε_Y (MWCNT)>(SWCNT): 3-4%;

(2) Activation volume on MWCNT is smaller (60%-70% of that on SWCNT);

(3) Crossover point of strain rate exponentially dependent on T, important for high temperature situations.

Load transfer on MWCNT





CNT: Nano Fibers

CNT to reinforce composites

- High Strength & High flexibility & Toughness & light-weight (Young's Modulus>1TPa)

- High aspect ratio L/D, can reach 1000

  Critical length: $L_c/D \sim \sigma_{max}/2\tau$

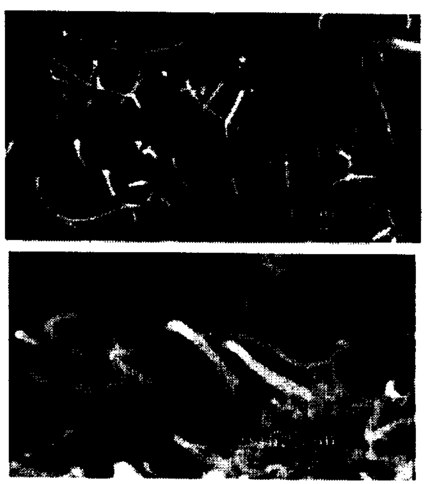
  - L_c: length of CNT; D: diameter of the CNT;
  - σ_{max} : tensile strength of CNT;
  - τ: interfacial shear stress

- Large surface area, good for bonding, adhesion

Polymer-CNT Composite

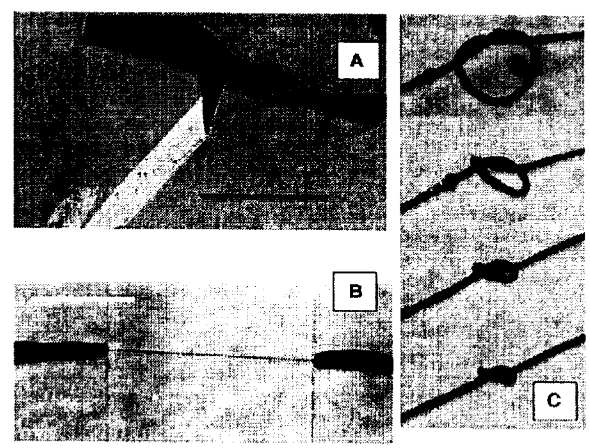
- *Structural and thermal properties*
- *Load transfer and mechanical properties*

SEM images of epoxy-CNT composite



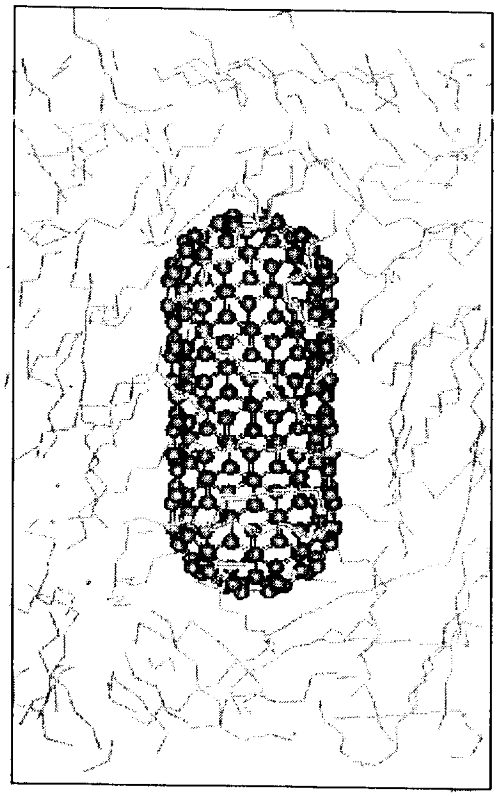
(L.S.Schadler et.al., Appl. Phys. Lett. V73 P3842, 1998)

SEM images of CNT fibers ribbon (processing in polyvinylacohol solution) & knotted CNT fibers



(B. Vigolo et.al., Science, V290 P1331, 2000)

MD Simulations of Polymer-CNT



Polymer-CNT composite

Simulation method

Classical MD: Tersoff-Brenner potentials for CNT, DLPOLY for polymer, and VDW interactions

System in simulation

Polyethylene & (10,0) CNT : (80 chains of PE relaxed by Monte Carlo methods, Np=10; 20A long CNT 8% volume ratio)

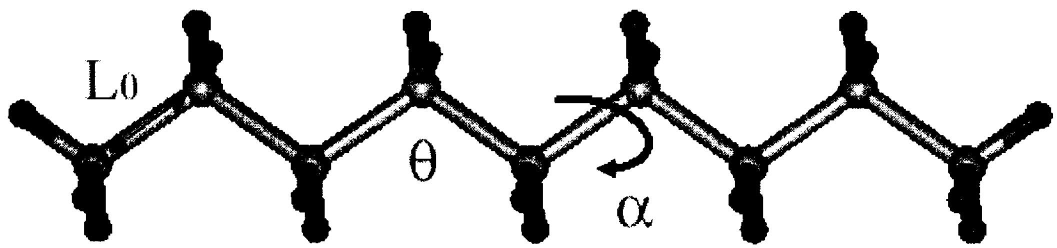
Preparations

Composites prepared at 300k; cooled down to 10K with rate 1K/1ps

composites change from liquid state through rubber state to glassy state

Force Field

Intramolecular potentials



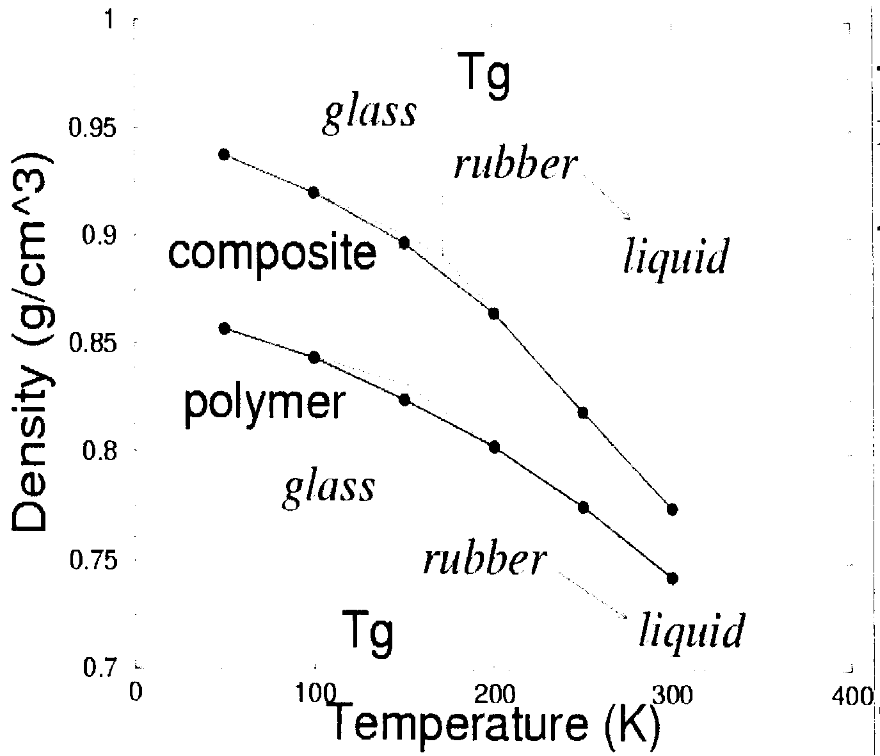
Valence angle potential: $\Phi(\theta) = 0.5k_\theta(\cos\theta - \cos\theta_0)^2$,

Torsion potential: $\Phi(\alpha)/\mathrm{J\cdot mol^{-1}} = C_0 + C_1\cos\alpha + C_2\cos^2\alpha + C_3\cos^3\alpha$,

Harmonic potential: $0.5\,k_b(l-l_0)^2$

Density Dependence on Temperature

Small system: L/D~2, Np=10



Results

-Glass transition temperature Tg increased from 150K to 175K

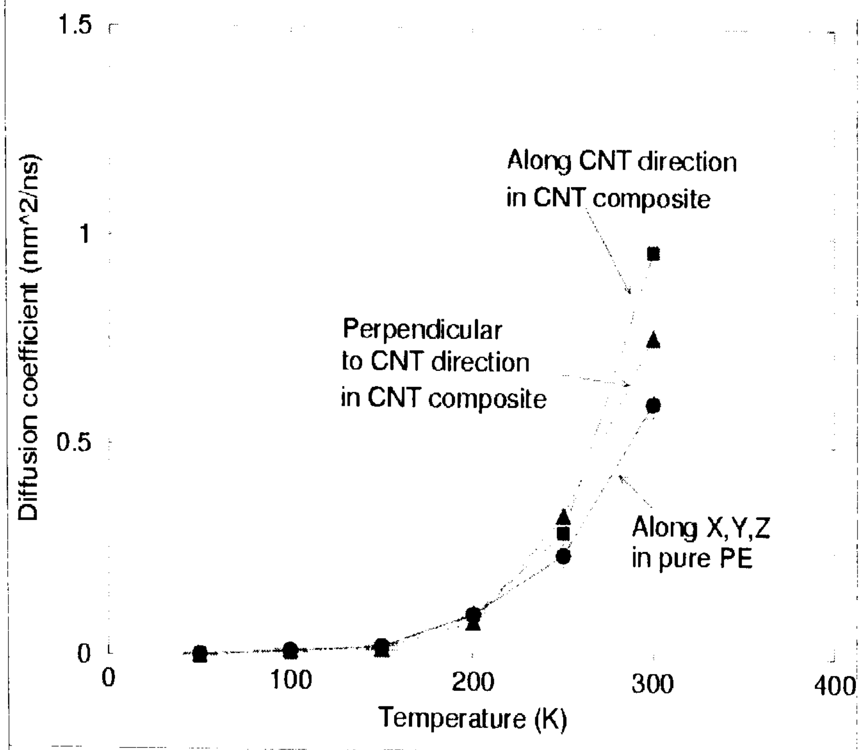
-Thermal expansion coefficients: (K^{-1})

	PE	PE-CNT	
$T<Tg$	3.8×10^{-4}	4.5×10^{-4}	↑18%
$T>Tg$	8.6×10^{-4}	12.0×10^{-4}	↑40%

(Experimental value: $1.0\times10^{-4}\,K^{-1}$; T <Tg)

Diffusion Coefficients

Small system: L/D~2, Np=10



Diffusion coefficients of polymer with CNTs embedded

Diffusion coefficient increased, especially along CNT axis direction, indicating enhancement of thermal conductivity

•Experiments on ABS/CNT & RTV/CNT show larger increase
(Rick Berrera's group at RICE)

(Ajayan's group at R.P.I. is investigating these subjects in detail)

* C. Wei, D. Srivastava, and K. Cho (Nano Letters, in press)

Modulus of Polymer-CNT Composites

(Halpin-Tsai's formula)

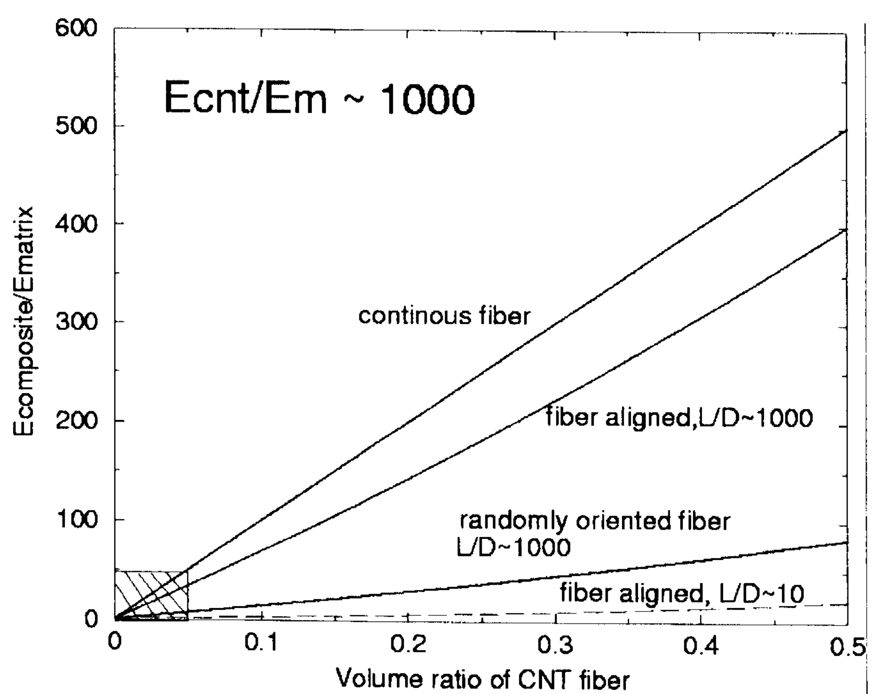
$$\boxed{\frac{E_c}{E_m} = \frac{1+\xi\eta V_f}{1-\eta V_f}}$$

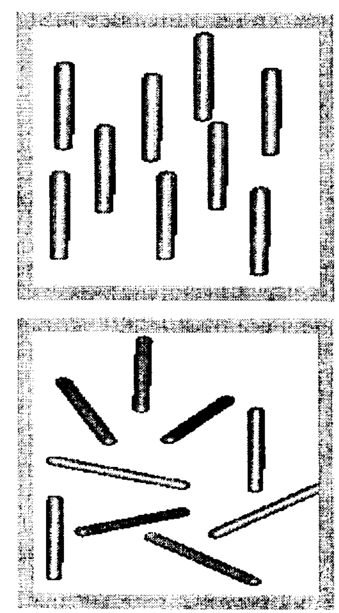
E_c, E_m, E_f :Modulus of composite, matrix and fiber

V_f : Volume ratio of fiber

$$\eta = \frac{(M_f / M_m - 1)}{(M_f / M_m + \xi)}$$

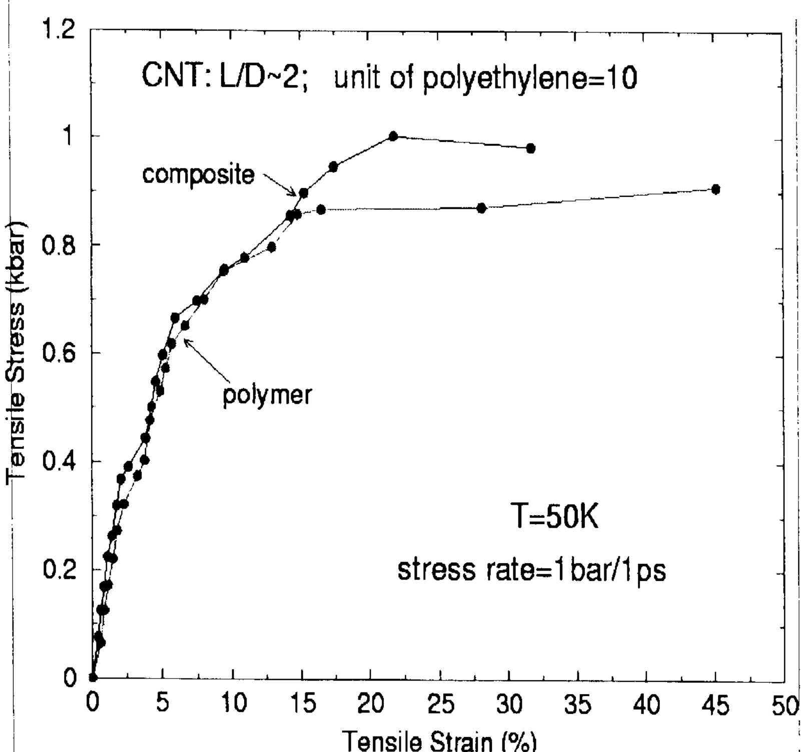
ξ: Dependent on geometry, packing of fiber; aspect ratio of fiber





Stress-Strain Curve & Load Transfer

Mechanical behavior of Composite:
Elastic region and Yielding



Enhancement of Young's modulus: 30%

Load transfer: within 0.7%

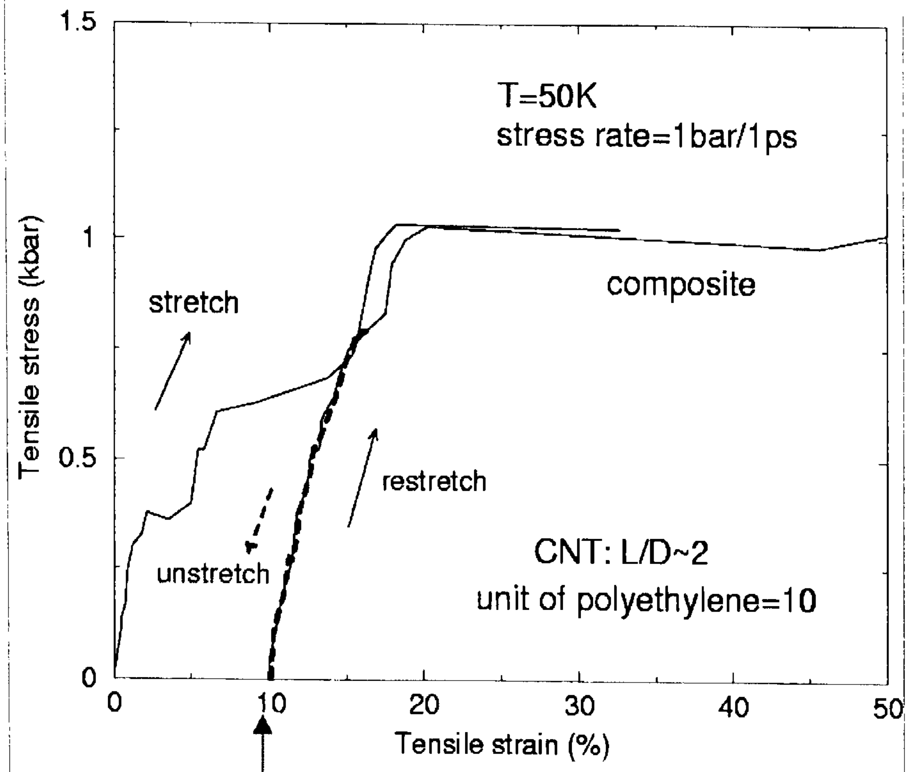
Poisson Ratio effect:

CNT ~ 0.1-0.2, Polyethylene ~ 0.44

Compression pressure perpendicular to tube axis contribute to improvement

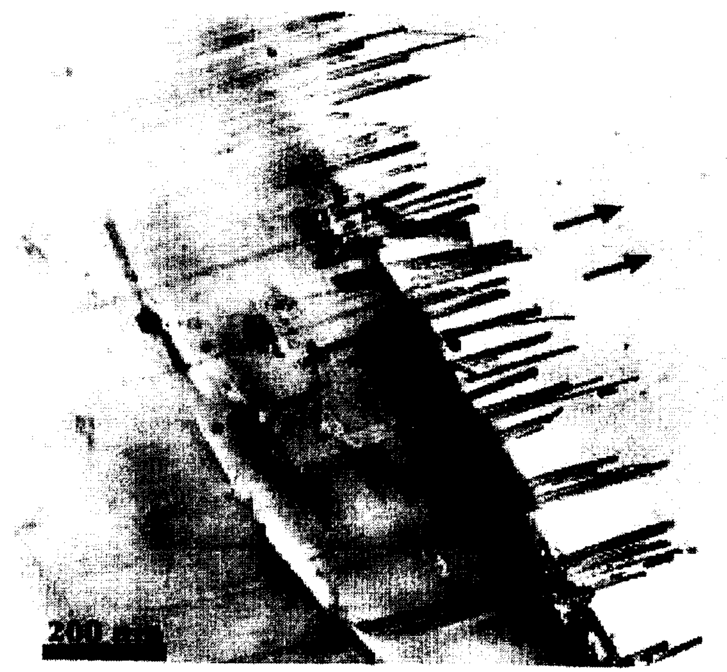
Loading Sequence

Work hardening of composite with stretching



•Residue strain

TEM images of alignment of CNTs in a polymer matrix by stretching



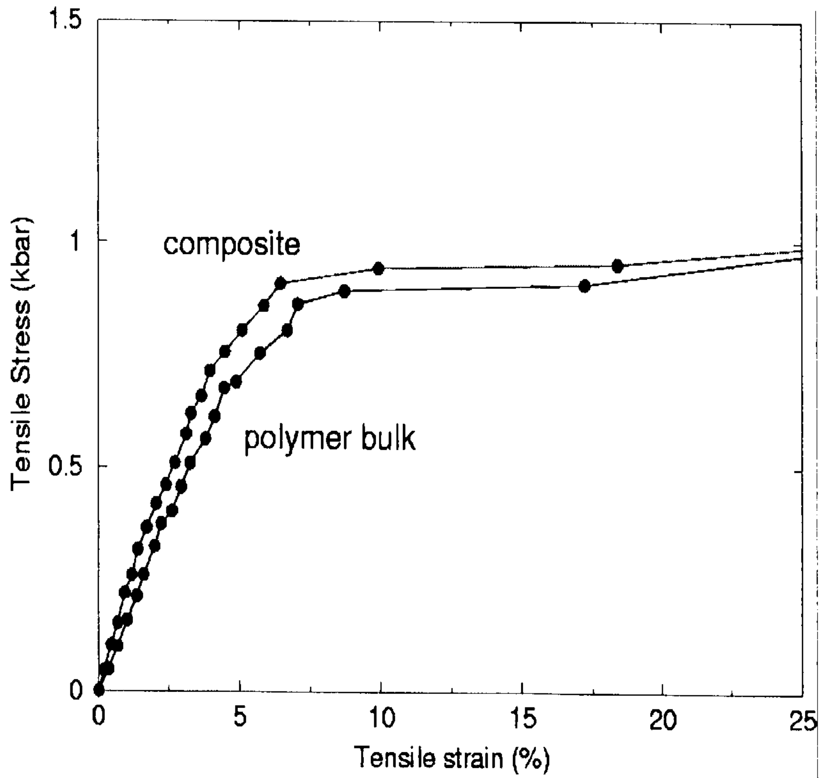
(L. Jin et.al., Appl.Phys. Lett., V73 P1197, 1998)

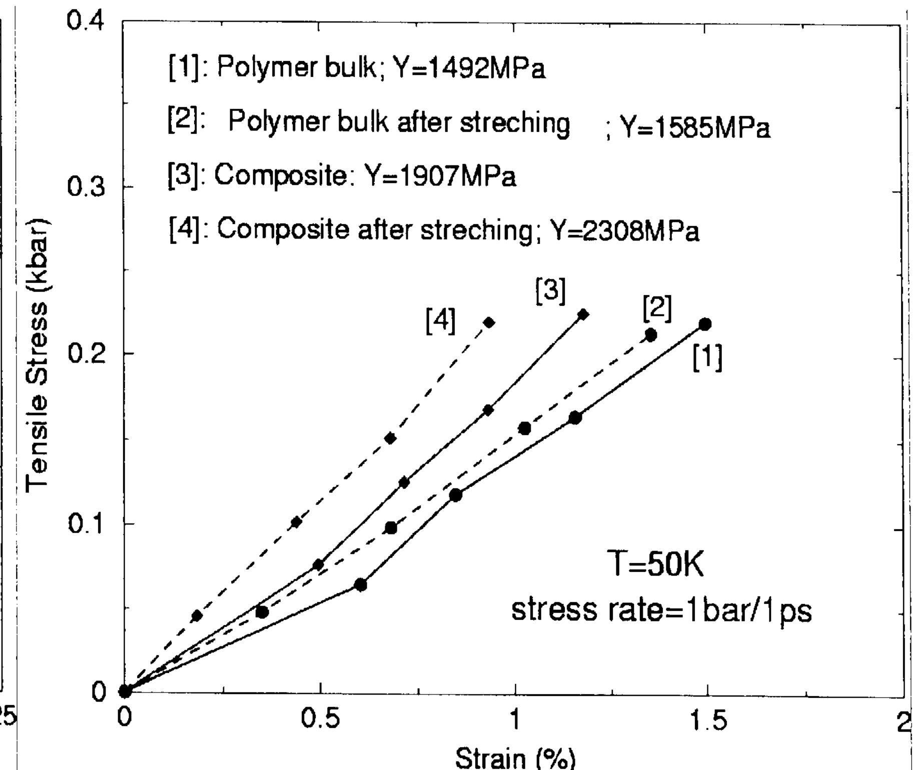
Young's Modulus

-Young's modulus of CNT composites 30% higher than polymer matrix

-Stretching treatments enhance Y by 50%

(L/D~2, Np=10)





Conclusions

- Yielding of carbon nanotubes strongly dependent on strain rate and temperature: transition state theory
- Polymer-CNT composite has larger thermo-expansion above Tg
  - Phonon modes and Brownian motion leading to larger exclude volume of embedded CNT
  - Diffusion of polymer matrix increased above Tg
- Young's modulus of composite enhanced by 30% through VDW interaction.
  - Load transfer happening within 0.7%; stiffness of CNT bond increases modulus of composite
  - Loading sequence can improve the enhancement of modulus of composite